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14. ABSTRACT Carbon fiber reinforced plastic (CFRP) structures are more and more utilized in high tech applications and especially in aviation due to their low weight and relatively high strength and stiffness. Introduction of porosity in the matrix resin system can achieve further reduction in weight while maintaining or improving properties and ultimate performance. This porosity can be achieved by using epoxy foams. Epoxy foam matrices are known to have many advantages such as high adherent strength, low water adsorption, good dimensional stability, heat resistance, and resistance to chemicals, in addition to impact improvements. Moreover, a particular advantage of epoxy foams is their tendency to inhibit crack propagation in composite materials. In this work, an effort to study process, mechanical, and morphological properties of foam matrices from the macro, micro, and nano perspective has been made. Foam evaluation to achieve higher toughness and inhibit crack propagation was investigated first by adding foaming agents such as styrene oxide during the curing process of epoxy based matrices, and second by introducing montmorillonite clays internally on the void surface of polyurethane foams. Finally, the effect of pressure during cure, independent of temperature, as a novel foaming process manufacturing technique, was also investigated and evaluated through differential scanning calorimetry and dynamic mechanical analysis.					
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Polymeric and Composite Systems

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EXECUTIVE SUMMARY

The research during the past years focused on the nano-modification of traditional polymeric matrix systems based on foaming part of the matrix in double pass impregnation processes. Furthermore, research has been performed for internally controlling the foaming pores with nano-additives. The pressure influence during the curing process, separated from temperature, has also been investigated as a new cost efficient manufacturing technique, assisting the cellular structures. Additionally, in the beginning of those two years all our activities were transferred from University of Delaware to our new wholly owned operations in Seattle, Washington. This effectively reconstituted a non-profit research institution, F.R.E.E.D.O.M., with the flexibility of a profit research and development organization, GloCal Network Corporation, with both entities doing business as the Polymeric Composites Laboratory. F.R.E.E.D.O.M. has also successfully received direct funds from the National Science Foundation for a series of international workshops that directly benefited this effort by establishing closer collaborations with related programs in the United States and abroad.

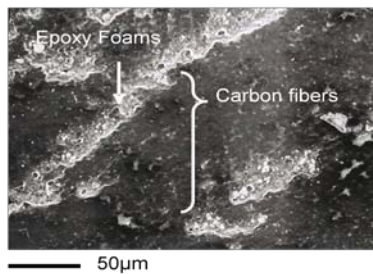
ACCOMPLISHMENTS

The performed research of carbon fiber reinforced composite materials with epoxy foams has accomplished an improvement of mechanical and morphological properties, when compared with traditional ones. In general, from a macro, micro and nano point of view, the void content due to matrix foaming can be calculated by the equation:

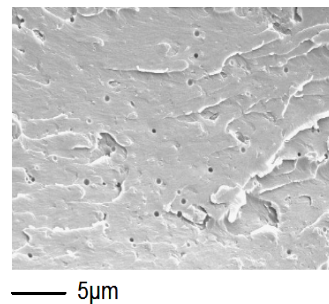
$$\text{Void content} = \left\{ \frac{D_c - D_f}{D_c} \right\} \times 100$$

In this equation, D_c is the average density of reference samples and D_f is the average density of CFRP foam samples.

1) Focusing on the characterization of the foaming materials, epoxy foam CFRP samples were manufactured, and then investigated by SEM and mechanical testing. A prepreg processing machine and an autoclave were used to manufacture samples. More specifically, two sets of samples were prepared with a difference in the pressure ramp-up and the hold of the autoclave.

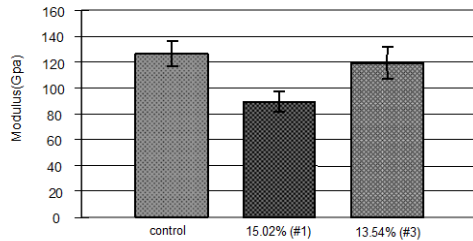


SEM photomicrograph of CFRP with epoxy foam as matrix

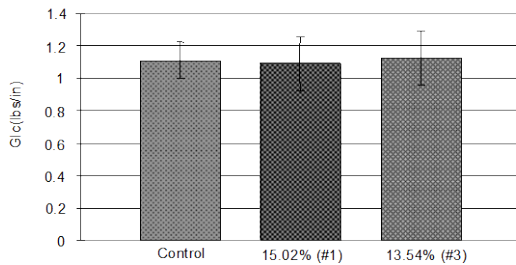


SEM photomicrograph of epoxy nano foams, 350x magnification

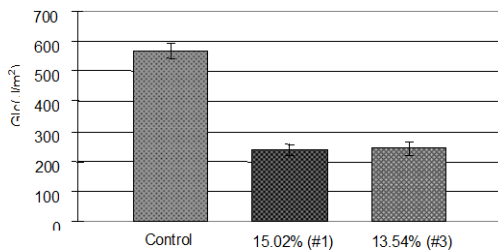
SEM photomicrographs showed that samples with a higher pressure ramp-up and lower styrene oxide content produced epoxy with nano scale foam diameters. In addition, according to the void content equation, the epoxy foam CFRP samples were reduced in weight by about 7% to 13%, compared to the reference samples. Mechanical testing in a 3-point bending mode showed no significant differences compared to the conventional CFRPs. Moreover, no differences were observed in Mode I fracture toughness testing. This may be attributed to the fact that crack propagation was inhibited by the presence of foam voids. However, as expected, Mode II fracture toughness was found to decrease with increased foam void content.



3-Point Bending test results

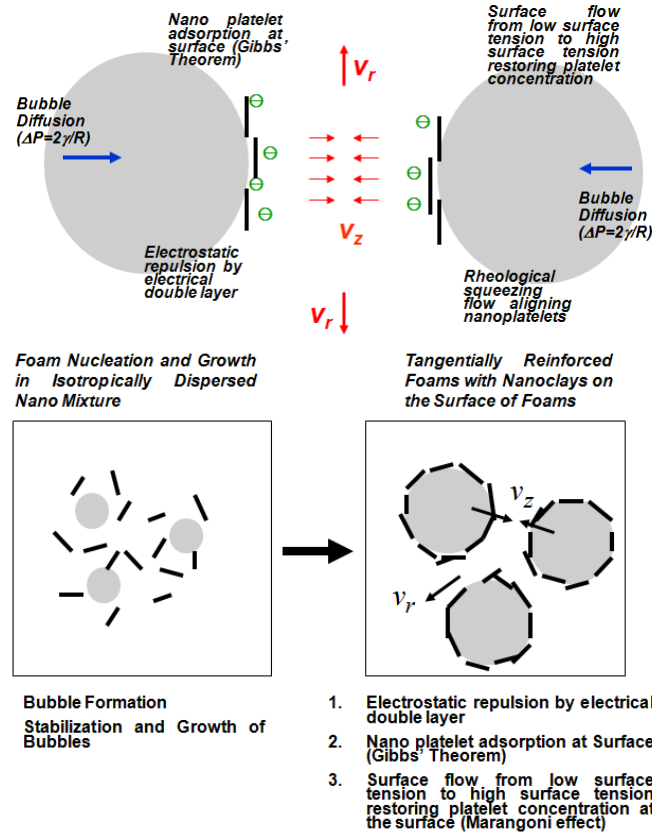


**Mode I Fracture Toughness (GIc)
Double Cantilever Beam (DCB) test
results**

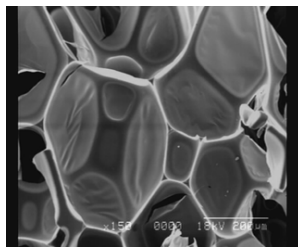


**Mode II Fracture Toughness (GIIc)
End Notch Flexure method (ENF) test
results**

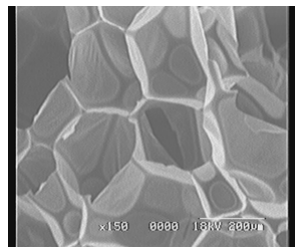
2) An effort was made to control void formation and size by adding nano-clays of montmorillonite in polyurethane foam with carbon preregs. SEM observation was performed on polymer samples, layered with urethane, and reinforced with different contents of nano-clays. Furthermore, the potential control of cellular structures by internally introducing nano-additives on pore surfaces has been investigated. Development of urethane foam layers reinforced by nano-clays of montmorillonite was a first step in this perspective. More theoretical work has been performed to explore the introduction of nano-fibers around the surface of epoxy foaming voids. This will be achieved in similar terms with the montmorillonite clays introduction to urethane layers.



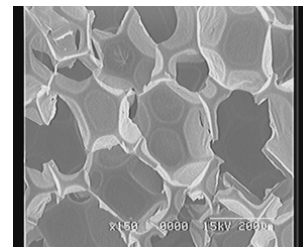
Furthermore, some SEM photos from the urethane layers reinforced with nano-clays of montmorillonite are presented in different nano-clays contents.



5% Nano-Clays



3% Nano-Clays



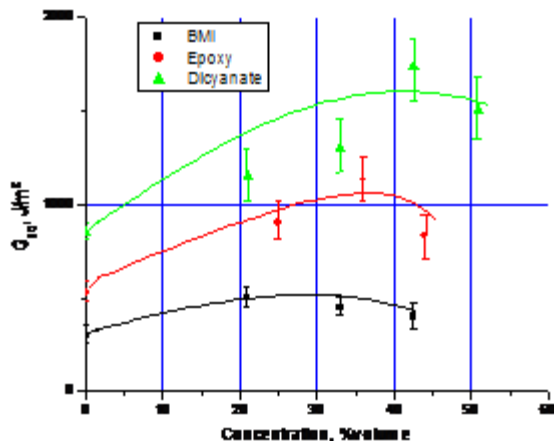
1% Nano-Clays

3) Moreover, work has been done on the interlayer toughening, and some of this work has been published regarding the fracture toughness interlayer. The comparison of Mode I and II interlaminar fracture toughness in three different CFRP resin model systems reinforced in the interlayer with Modified Nylon Spherical Particles has been investigated. The three resin systems were epoxy, dicyanate and BMI with dicyanate being less brittle than epoxy and BMI being more brittle than epoxy. Conventional structure laminate results demonstrate that the dicyanate is the toughest resin system and the BMI is the most brittle with G_{IIC} unmodified values of 800, 500 and 250 J/m² for dicyanate, epoxy and BMI respectively. All three systems show dramatic improvements in G_{IIC} , with a maximum occurring for each system that shifts towards higher

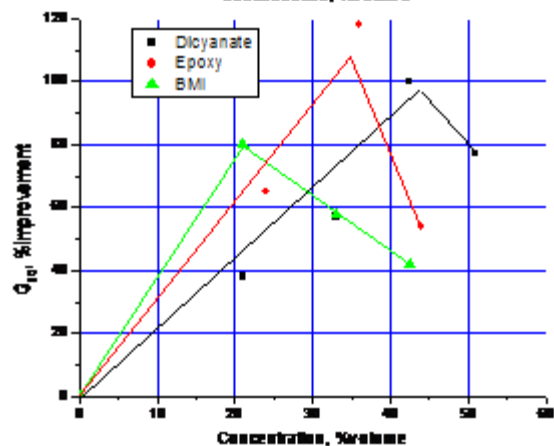
concentrations as the host resin toughness increases. When crack propagation moves from the interlaminar region to the intralaminar region, a maximum G_{IIC} occurs.

The comparison of ENF results for the three model systems demonstrates that the host resin base toughness plays an important factor in the final layered structure toughness. Dicyanate, which is the toughest resin system, has the toughest multilayer laminate. BMI, which has the least tough resin system, has the least tough multilayer laminate. By plotting the ENF results as a percent G_{IIC} improvement, it is interesting to mention that all three systems present similar improvements in toughness. BMI produced a maximum improvement of 80%, epoxy produced an improvement of 118% and dicyanate produced an improvement of almost 100%. BMI G_{IIC} improvement may be slightly low due to some voids in the fracture samples.

Despite the fact that the toughness improvements of the three systems are similar, the maxima do not occur at the same modifier particles content levels. The BMI maximum occurs at 21% modifier particles, the epoxy maximum occurs at 36% modifier particles and the dicyanate maximum occurs at 42%. Consequently, the more brittle the resin system, the lower the maximum concentration of modifier particles required to obtain similar toughness improvement.



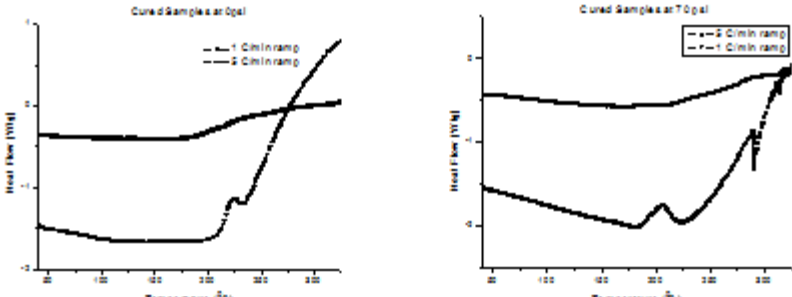
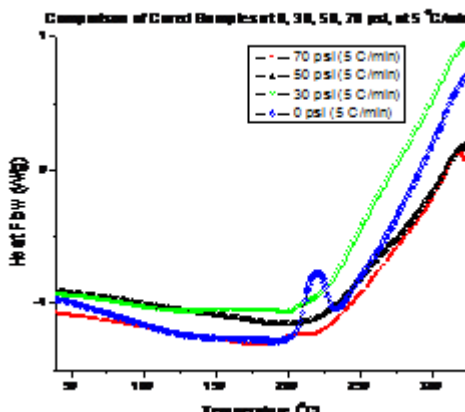
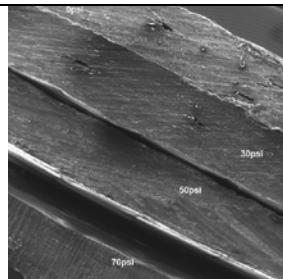
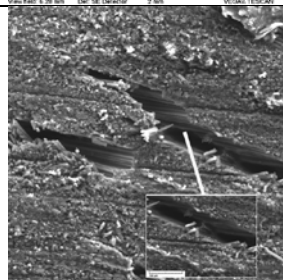
Mode II Interlaminar Toughness (G_{IIC}) Comparison of Epoxy, Dicyanate and BMI Based Model Systems as a function of Modifier Particle Concentration in Interlayer

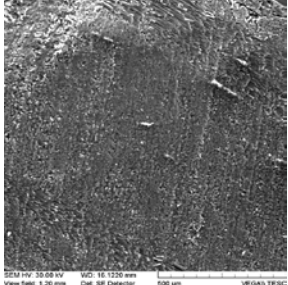
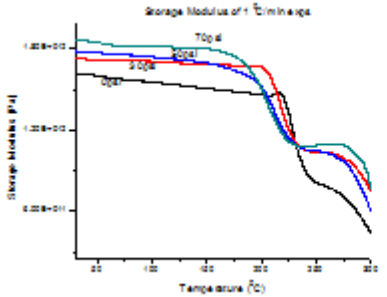
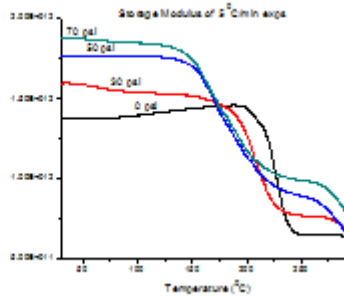
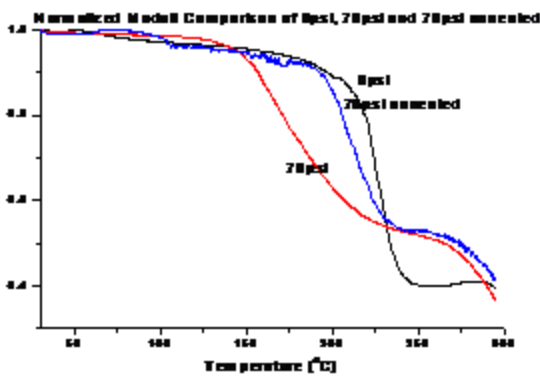


Percent Mode II Interlaminar Fracture Toughness Improvement of Epoxy, Dicyanate and BMI Model Systems as a function of Modifier Particle Concentration in Interlayer

4) Another field in which work has been performed is manufacturing prepreg panels through pressure variation in a repairclave, separating out pressure from

temperature. Evaluation of the manufacturing results was done using Differential Scanning Calorimetry, Dynamic Mechanical Analysis, and Scanning Electron Microscopy. For conventional epoxy CFRPs manufactured in the Repair Clave with the same temperature profile, pressure was varied at 0, 30, 50 and 70 psi. Following are figures demonstrating the results from DSC, DMA and SEM.

DSC		
		DSC dynamic scans at 1 and 5 °C/min for different pressure cases (Left. 0 psi, Right. 70 psi)
		Storage modulus of carbon fiber prepreg – 8 plies manufactured at 0, 30, 50 and 70 psi, and at 1 and 5 °C/min
SEM		
		The different samples manufactured using different pressures (10, 30, 50, and 70 psi, from top to bottom)
		A sample manufactured at 0 psi, showing increased void formation

		<p>The entire thickness cross section of a sample manufactured at 70 psi, showing much less void formation</p>
DMA		
		<p>Storage modulus of carbon fiber prepreg – 8 plies manufactured using 0, 30, 50 and 70 psi, at 1 and 5 °C/min</p>
	<p>Normalized Moduli Comparison of 0psi, 70psi, and 70psi annealed. T_g of the annealed 70 psi sample at 220 °C is much closer to that of the 0 psi sample.</p>	

In SEM observation, it can be seen that 0psi samples have much higher void formation than the 70psi samples. Also the SEM results show that void formation is inversely related to the pressure employed during manufacturing.

DMA verifies SEM findings as it can be seen that there is a slight increase in modulus while manufacturing pressure increases. This is to be expected as the higher the pressure, the less void formation within the composite. However, it is observed that glass transition temperature slightly decreases while the pressure increases. The glass transition reduction using a 1 °C/min heating rate is in the order of around 30 °C ($T_g = 206$ °C at 70 psi and $T_g = 228$ °C at 0 psi). This difference expands when the heating rate increases to 5 °C/min, to be in the order of around 50 °C ($T_g = 180$ °C at 70 psi and $T_g = 225$ °C at 0 psi). This finding can be explained due to the internal stresses that the higher pressure imports into the composite. Thus, the temperature increase relieves the stresses and the material softens, leading to an apparent decrease of the glass transition temperature. This was verified by annealing the 70 psi manufactured samples at 220 °C for an hour, and then performing DMA at a 5 °C/min heating rate. The T_g value was increased from 180 °C to 214 °C, which is a value very close to that of the 0 psi manufactured sample.

NEW FINDINGS

While at the Universities of Washington and Delaware, Professor Seferis has neither applied for, nor received any patents, either personally or through his affiliated institutions. All his work is published in the open literature, and he works with companies that implement his work in products and processes.

PERSONNEL SUPPORTED

1. P.I. involved in the research project:

Dr. James C. Seferis

2. Professionals

Dr. Chris N. Velisaris

Ari J. Vihersaari

David C. Bowes

3. Graduate Student Interns

Vassilis Drakonakis

Aris Sfakianakis

PUBLICATIONS

1. Ishiguro, K., Velisaris, C.N., Vihersaari, A.J., Seferis, J.C., Kim, D., and Nam, J.D., "Matrix Resin Content Influences on Carbon Fiber Reinforced Polymeric Systems," Society for the Advancement of Material and Process Engineering (SAMPE) 52nd International Technical Conference, Baltimore, Maryland, June 3-7, 2007.
2. Seferis, J.C., "Polynanomers and Polynanomeric Composites: From Concept to the Design, Analysis, and Construction of Load Bearing Aircraft Structures," International Conference on Structural Analysis of Advanced Materials, Patras, Greece, September 2-6, 2007.
3. Drakonakis, V.M., Ishiguro, K., Velisaris, C.N., Seferis, J.C., and Papanicolaou, G.C., "Layered Hybrid Matrices for Carbon Fiber Reinforced Composites," Society for the Advancement of Material and Process Engineering (SAMPE) Technical Conference, Long Beach, California, May 18-22, 2008 (in press).
4. Drakonakis, V.M., Dillman, S.J., Nam, J.D., Papanicolaou, G.C., and Seferis, J.C., "Kinetic Viscoelasticity Modeling Applied to Degradation during Carbon-Carbon Composite Processing," Proceedings International Astronautical Conference, November 2008 (in press).
5. Drakonakis, V.M., and Seferis, J.C., Wardle B. L., Nam, J.D., Papanicolaou, G.C., "Kinetic Viscoelasticity Modeling Applied to Degradation during Carbon-Carbon Composite Processing," Acta Astronautica Journal, Glasgow Edition, (Submitted, January 2009).

6. Drakonakis V. M., Ancuta C. G., Seferis J. C., Casterline E., Lewis M., Woods R., Wardle B. L., Doumanidis C. C., Papanicolaou G. C., "Effects of Curing Pressure on Structural Polymeric Composites for Commercial Aviation Cured Without Autoclave," International Conference on Structural Analysis of Advanced Materials 2009, September 7-10, Tarbes, France, 2009 (Accepted).
7. Drakonakis V. M. and Seferis J. C., Wardle B. L., Nam J. D., Papanicolaou G. C., Doumanidis C. C., "Analysis of Carbon Carbon Pyrolytic Processes through Kinetic Viscoelastic Modeling," Journal of Advanced Materials, (Submitted, April 2009).
8. Drakonakis V. M., Velisaris C. N., Seferis J. C., Doumanidis C. C., Wardle B. L., Papanicolaou G. C., "Matrix Hybridization in the Interlayer for Carbon Fiber Reinforced Composites," Polymer Composites Journal, (Submitted, April 2009)

HONORS AND AWARDS

On June 15, 2005, Professor Seferis retired from the University of Washington and assumed an interim position as Research Professor at the Center for Composite Materials at the University of Delaware through December 31, 2006. He has reconstituted his laboratory, the Polymeric Composite Laboratory, first established at the University of Washington in collaboration with aerospace, chemical, and materials industries, in private facilities in Seattle, Washington. Professor Seferis and his team of full time professionals continue their research and development activities adding formally to their collaborative work with universities from the United States and abroad (Europe and Asia). He is still in demand for presenting his work, especially that funded by the AFOSR, of which he presented as keynote lecturer in meetings and colloquia during this funding period. These included both the 2007 and 2008 SAMPE Annual and Technical Conferences; a U.S.-Greece Bilateral Meeting; the International Conference on Structural Analysis of Advanced Materials (2007 and 2009); an MIT-Aeronautics Department Colloquium, the Japanese Conference on Composites and the Environment; CACRC workshops in Greece and Wichita (2007 and 2008); GloCal workshops in Seattle, Paris and Athens (2007 through 2009); and International Astronautical Conferences (2007 and 2008).